Anna Vasileva

Ion exchange for natural organic matter removal

Ion exchange resin comparison

Helsinki Metropolia University of Applied Sciences
Bachelor Degree

Environmental Engineering

Thesis

May 2014

Metropolia

Abstract

Author(s) Title Number of Pages Date	Anna Vasileva Ion exchange for natural organic matter removal 32 pages 10 May 2014
Degree	Bachelor of Engineering
Degree Programme	Environmental Engineering
Specialisation option	Water treatment technology
Instructor(s)	Kaj Lindedahl, Principal Lecturer Mohammad Mahdi Bazri, M.A.Sc., Ph.D. Candidate, Project Supervisor Madjid Mohseni, Ph.D., Project Supervisor

The purpose of this thesis was to evaluate the efficiency of different types of ion exchange resins in terms of natural organic matter (NOM) removal from drinking water.

The experimental part of this project was done at the facilities of the University of British Columbia, Vancouver, Canada. The project is a part of comprehensive study of IEX resin for NOM removal conducted at the Engineering and Biological Department of the University.

Several experiments on resin saturation and regeneration were performed. The multiple loading tests were conducted for resin saturation. Seven loadings were applied to saturate the resin, which was equivalent to 700 bed volumes. During experiments samples were taken and analyzed for NOM residuals with a by spectrophotometer and a TOC analyzer.

A strong basic resin and a weak basic resin were compared in terms of performance. Both resins were compared in two different forms: OH^- and Cl^-. Of the four resins the strong basic resin in Cl^- form showed the most consistent percentage of NOM removal from the samples; moreover, it showed the highest percent of removal at the point of 700 BV. The result of the strong basic resin regeneration experiments showed higher productivity of Cl-form resin than OH-form resin, although among the weak basic resins the resin in OH-form was more productive than the resin in Cl-form.

The findings of this thesis can be applied to producing a pilot-scale installation. Further research is needed to evaluate the resin performance in larger scale.

Keywords	Ion exchange, NOM removal, ion exchange resin, water treatment, resin saturation, resin regeneration, TOC, UV254

Acknowledgments

This study was conducted under the RES'EAU-WaterNET foundation, which is the organization devoted exclusively to developing innovative water treatment technologies for small, rural and first nation communities in Canada. The experimental part was done at the laboratory of the Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, Canada.

The growing interest about the ion exchange process for water treatment, the positive impact on the environment and the fact that the achieved results could be applied to the industrial scale installations, fueled my curiosity to obtain more information on the issue. I have gained a wide spectrum of knowledge in ion exchange theory, experimental data analysis and skills in laboratory testing.

I would like to take this opportunity to express my immense gratitude to all those persons who have given their invaluable support and assistance. In particular, I am profoundly indebted to my supervisor, Doctor Madjid Mohseni, P.Eng., Scientific Director of RES'EAU-WaterNET and to my supervising researcher, Doctorate Candidate Mohammad Mahdi Bazri. The supervision was performed with the highest level of professionalism and knowledge in the field of study.

I would like to thank George W. Thorpe, the member of Board of Directors of RES'EAU-WaterNET, who made a great effort to help me come to Canada and participate in the project.

I would like to thank Helsinki Metropolia University of Applied Sciences for the financial support of the trip to Canada and my teachers, in particular Mr. Kaj Lindedahl, who was very generous with his time and knowledge and assisted me in each step to complete the thesis.

I would also like to thank my family and colleagues for their constant encouragement of my endeavours. Special thanks go to my husband, Vasilev Konstantin, who believed in me and was always supportive.

List of abbreviations

BV	bed volumes
DBPs	disinfection byproducts
DOC	dissolved organic carbon
IC	inorganic carbon
IEX	ion exchange
NDIR	non-dispersive infrared detector
NOM	natural organic matter
QA	quaternary ammonium
SR	Suwannee River
TC	total carbon
TOC	total organic carbon
UV-Vis	ultraviolet visible

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1 Introduction

Availability of drinking water is essential for all living organisms on the planet. Natural organic matter (NOM), naturally presented in the surface water, is one of the concerns about drinking water since those substances can affect its quality with such problems as taste, color, odor and biological growth in water distribution system [1]. Moreover, NOM reacts with chlorine to form halogenated organic disinfection byproducts (DBPs) that cause human health problems. Choosing an appropriate method for NOM removal from drinking water has become an important issue.

The most common approach for NOM removal from drinking water is the conventional water treatment sequence of coagulation, flocculation, clarification, and filtration. However, this method does not present a solution for the specific problems. According to Boyer [1], anion exchange technology has the potential to be a more specific and effective treatment process for the removal of NOM.

The purpose of this thesis was to investigate the ion exchange (IEX) method with respect to NOM removal. To this end, the efficiency of different types of ion exchange resins to reduce the dissolved organic carbon (DOC) in synthetic water was evaluated and compared. The synthetic water used in the thesis emulated the main components of river water. NOM extracted from the Suwannee River (SR) water, southern Georgia, USA was applied for that purpose. Aquatic NOM is derived from both the breakdown of terrestrial plants and as the byproduct of bacteria, algae, and aquatic plants. The SR is an example of a terrestrial end-member environment. SR NOM is characterized by high aromatic carbon content and is of predominantly lignin origin [1].

The effect of the IEX process on NOM reduction in drinking water has been studied extensively in recent years. According to the studies conducted, the IEX method considered to be an effective method for the dissolved organics removal. Drikas, Dixon and Morran [2] concluded that the water pre-treatment by using IEX prior to conventional treatment results in consistently greater removal of NOM in the treated water than the same processes without IEX.

The effectiveness of NOM removal depends on its physical and chemical processes. Humbert [3] reported that NOM with the molecules of high molecular weight are removed more effectively by coagulation, whereas IEX resin is more sensitive for low molecular weight molecules than the conventional treatment technologies. Thereby, the IEX process can be used as complimentary to coagulation and by that reduce the amount of coagulant used for the treatment process.

The comparison of effectiveness of different types of resin has been reported by Cornelissen [4], but the regeneration of the resin was not taken into account, whereas in this thesis project both saturation and regeneration abilities of the resins were investigated.

The aim of the thesis project was to compare two ion exchange resins, a strong basic resin and a weak basic resin, and to evaluate the efficiency of the resins in two different forms, CL^- and OH^-.

This thesis has a potential significance; the obtained results of the experiments might be used for identifying an efficient way of water purification by using ion exchange resin. The outcome of the thesis might be interesting for the resin manufacturers and for water treatment companies and could be applied for adjusting the performance of water treatment processes.

The remainder of this paper is divided into the following chapters:

Chapter 1 presents the theoretical background of the Ion Exchange process in general; introduces NOM, its structure and effect on the environment and human health; and defines the analysis methods of the treated samples.

Chapter 2 describes the ion exchange technology for water treatment process and for natural organic matter removal in particular. The properties of IEX resin and reproduced water utilized for the experiments are listed and described.

Chapter 3 explains the experimental methodology used in this thesis: resin saturation and regeneration procedures, sampling protocol.

Chapter 4 introduces the methods applied for data analysis of the samples collected during the experiments.

Chapter 5 presents the results obtained during the experiment and analyses as well as compares them.

In chapter 6 the main findings of the thesis are highlighted and conclusions are drawn.

2 Theoretical background

This chapter covers the nature of organic matter (NOM) components that have to be removed from river water meant for drinking purposes and depicts the ion exchange mechanism which is the basis of the method used for NOM removal. The identification of these organic matters distinguished utilizing UV spectroscopy. The basics of analytical techniques of UV spectroscopy and TOC used to quantify the residual NOM are described.

2.1 NOM

Natural organic matter is naturally present in surface waters. It is a complex mixture of organic components, such as humic and fulvic acids, low molecular weight acids, proteins and amino acids, and carbohydrates, which are present in varying degrees in all drinking water sources [4].

In late 1980s, an increase in color (NOM) was first reported in Swedish surface waters (Forsberg and Petersen, 1990). During the last few decades, several other reports confirm that NOM occurrence in water is a worldwide phenomenon. Change in the climate (temperature, quality, and amount of precipitation) and the decline in acid deposition are reasonable explanations for the increasing NOM concentrations [5].

According to Matilainen [5] and Kornegay [6], several challenges are posed by the presence of NOM in drinking water:

- NOM reacts with disinfectants such as chlorine, chloramines and ozone to form disinfection by-products (DBPs), many of which are suspected to pose toxicological hazards.
- NOM increases water treatment costs by increasing the dosage of coagulant used to remove organic substances, measured as total organic carbon (TOC), during the coagulation process.
- NOM causes water quality degradation in the distribution system due to the difficulties of its biodegradable and soluble fractions removing during the water treatment process.

- NOM may be one of the reasons of earthy-musty tastes and odors that are of aesthetic concern to water utilities [6].
- NOM increases the levels of complexed heavy metals and adsorbed organic pollutants [5].

The DBP formation is a major concern since it has a potential health effect. According to Environmental Protection Agency of the United States [7], numerous toxicological studies have been conducted on byproduct. These studies have shown several disinfection byproducts to be carcinogenic in laboratory animals (e.g., including bromate, certain trihalomethanes and haloacetic acids). Some disinfection byproducts have also been shown to cause adverse reproductive or developmental effects in laboratory animals (e.g. chlorite and certain trihalomethanes and haloacetic acids). An extensive research is being conducted at the moment to identify the potential health effect of disinfection byproducts. Due to all the problems that can be caused by the extensive amount of natural organic matter in drinking water it is necessary to remove those substances from the water.

There are several methods and techniques, which have already been applied in large scale on the industrial sites. Although the most efficient and economically feasible technique is still under determination, researchers have in recent years become increasingly interested in comparing different methods of NOM removal from drinking water.

2.2 Introduction to ion exchange

As it was mentioned above, NOM can be removed from raw drinking water by a sequence of coagulation, flocculation, clarification, and filtration methods. However, an extensive amount of research shows that anion exchange resin, the subject of this thesis, has high selectivity for NOM compounds.

Ion exchangers have many appearances: natural and artificial; inorganic and polymeric. They are woods, papers, sands, clays, glauconties, zeolites, functional resins, and even living organisms.

Chemical interactions could be different for different polymeric and inorganic ion exchanges. However, most of the thermodynamic and kinetic approaches, as well as the practical methods and technologies are essentially the same.

The exchange of cations as a phenomenon was first discovered in the nineteenth century in the experiments with soils. Natural cation exchangers have been known, but they were not widely used for almost a century until 1930 when the first organic ion exchangers were synthesized. Contrary to the exchange of cations, anion exchange was developed almost exclusively with synthetic organic resins. No natural anion exchangers with satisfactory properties were available before the synthetic anion exchange resins were invented [8].

2.3 Basic principles of the IEX mechanism

Ion exchange (IEX) is a process in which ions in a liquid phase (an electrolyte solution) exchange with ions in a solid phase (a solid ion exchange medium) [9].

Ion exchange is inherently a stoichiometric process. Any counter ions which leave the ion exchanger are replaced by an equivalent amount of other counter ions. This is a consequence of the electoneutrality requirements. When a counter ion moves out into the solution, the ion exchanger is left with an electric surplus charge which it must compensate for by taking up another counter ion. The total counter-ion content thus remains constant, irrespective of ionic compensation (see Figure 2.1) [10].

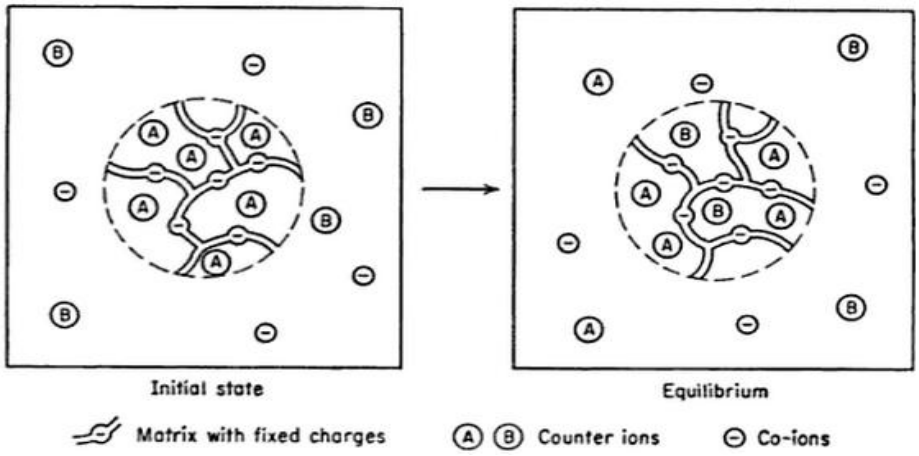

Figure 2.1. Ion exchange with a solution (schematic). A cation exchanger containing counter ions A is placed in a solution containing counter ions B (left). The counter ions are redistributed by diffusion until equilibrium is attained (right) [10].

The Ion exchange reaction can be described by the following equation, where ion exchanger M^-A^+, carrying A^+ cations as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations:

$$\underset{\text{Solid}}{M^-A^+} + \underset{\text{Solution}}{B^+} \rightleftharpoons \underset{\text{Solid}}{M^-B^+} + \underset{\text{Solution}}{A^+} \text{ [11]}$$

One of the absolute advantages of ion exchange over conventional treatment methods is that IEX is a reversible process; according to the manufacturer's specification, the saturated resin can be regenerated and utilized over several cycles. Although the regeneration process is effective and resin can be reused repeatedly, resins are commonly regenerated only to about two thirds of the total capacity.

During the regeneration, the captured ions are reconverted to their original form. Caustic soda, or sodium hydroxide (NaOH), and brine solution are used to regenerate the anion resin. A concentration of 4% sodium hydroxide and 10% sodium chloride are applied.

2.4 Methods for NOM residual analysis

Ultraviolet (UV) absorbance at 254 nm (UV_{254}) and total organic carbon (TOC) are commonly used to characterize water samples of NOM [1].

2.4.1 UV-Vis analysis method

Most ultraviolet–visible spectroscopy (UV-VIS) spectra are obtained by measuring the intensity of the absorption of monochromatic radiation across a range of wavelengths passing through a solution in a cuvette. The practical wavelength region extends from 190 – 400 nm (UV range) and from 400 – 780 nm (VIS range) [12]. Organic substances absorb UV light at wavelengths between 100 and 400 nm [13].

It is clear from many studies conducted that for the drinking water analysis, the UV absorbance at 254 nm wavelength is optimal to use to detect NOM compounds. The aromatic or unsaturated organic compounds, which represent the greater part of NOM, are having the highest absorption of the UV light at this wavelength. UV254 is directly

proportional to the concentration of aromatic and unsaturated carbon within NOM, and has been shown to be a useful surrogate for the concentrations of DOC and DBPs precursors in raw drinking water [1].

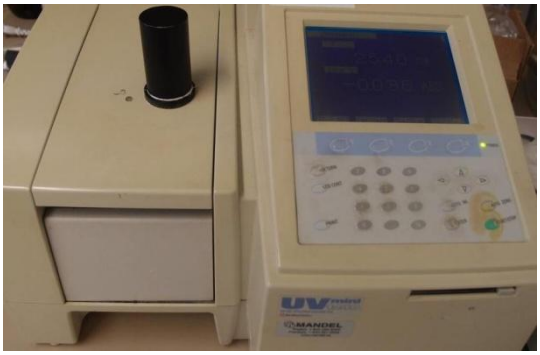

Figure 2.2. UV-VIS Spectrophotometer Shimadzu UV-Mini 1240.

In this thesis project, the UV-Vis spectrophotometer (Shimadzu UV-Mini 1240, see Figure 2.2) was utilized to analyze the UV absorption of the samples.

2.4.2 TOC method

Total organic carbon is a measurement for quantifying the organic carbon compounds in the drinking water. TOC measurements include suspended particulate, colloidal, and dissolved organic carbon (DOC) [13]. The DOC concentration is equal to >90% of the TOC concentration for most natural waters [1]. TOC in source waters comes from decaying natural organic matter (NOM). About 50% of NOM consists of TOC. Thus, the amount of NOM removed from the water during ion exchange process corresponds to the amount of TOC removed from this water. TOC quantity is expressed in units of mg/L.

TOC measurements have been adopted in various fields as an accurate quick indicator of total organic content [14]:

- Study and monitoring of organic contamination of rivers, lakes, dams, and other water in the natural water cycle;
- Water quality control of industrial effluent and sewage plant effluent and operation management for effluent processing;
- Process control of the organic content in water at all types of factories;

- Environmental and biotechnology research and R&D at test organizations;
- Study and monitoring of the degree of contamination of soil, sludge, and sediments;
- Control of purified or recycled water for the semiconductor, pharmaceutical, water-washing system, or nuclear power industries.

TOC does not identify specific organic constituent, although it gives reliable information about the presence of carbon-bearing molecules, corresponding to the NOM content in the water. TOC is a measure of all organic carbon atoms covalently bonded in the organic molecules occurring in a water sample. Total organic carbon consists of total carbon (TC) and inorganic carbon (IC, or carbonate), and the typical technique to measure TOC is subtraction of IC from TC [15].

Most TOC analyzers works by measuring the CO_2 released during the oxidization of organic carbon organic to determine the total organic carbon level [16].

Figure 2.3. TOC analyzer [17].

In this thesis project TOC measurements were made using the combustion catalytic oxidation method. The Shimadzu TOC-V_{CPH} analyzer (see Figure 2.3) was utilized to conduct the samples' analysis. The measurement principle of the Shimadzu TOC-V_{CPH} equipment is described below The TOC-V_{CPH} measurement flow line diagram is available in Figure 2.4 below.

TOC measurements made by combustion catalytic oxidation/NDIR method are described below:

1. Total Carbon Measurement

Carrier gas (purified air) is passed at a controlled flow rate of 150 mL/min through an oxidation catalyst-filled TC combustion tube, heated to 680°C. When the sample pre-treatment/injection system injects the sample into the combustion tube, the TC in the sample is oxidized or decomposes to create carbon dioxide. The carrier gas carrying the combustion products from the combustion tube is cooled and dehumidified in the dehumidifier before passing via the halogen scrubber into the sample cell of the non-dispersive infrared detector (NDIR), where the carbon dioxide is detected. The NDIR analog signal forms a peak, and the data processor calculates the peak area. To measure the TC concentration of the sample, the relationship between the TC concentration and peak area (calibration curve) is predetermined using a TC standard solution, to express the peak area as a ratio of the TC concentration.

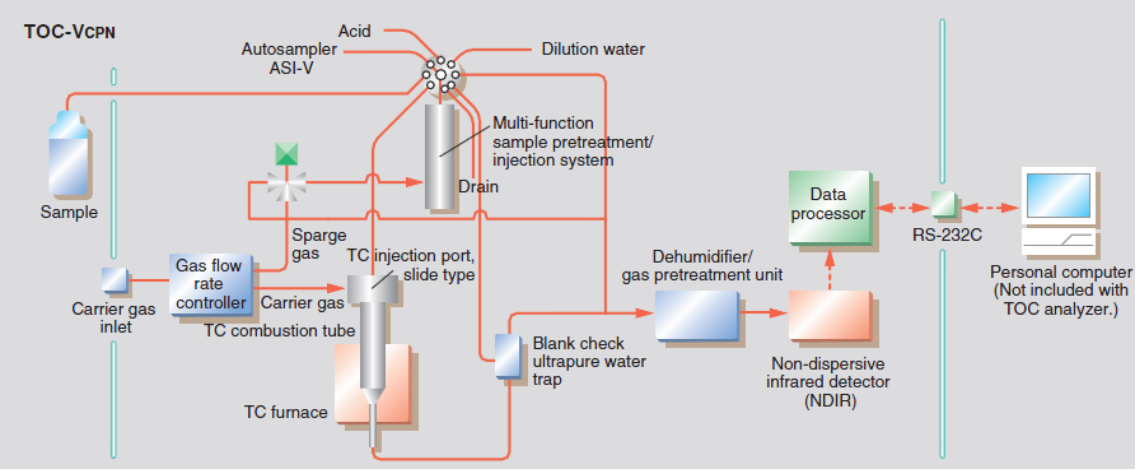

Figure 2.4. Measurement flow line diagram

2. IC (Inorganic Carbon) Measurement

The acidified sample is sparged with the carrier gas (purified air) to convert only the IC in the sample to carbon dioxide. This carbon dioxide is detected by the NDIR, and the sample IC concentration is measured in the same way as TC.

The IC is a combination of carbonate and bicarbonate.

3. TOC (TC-IC) Measurement

Subtracting the IC concentration from the TC concentration determines the TOC concentration [14].

3 Ion exchange for natural organic matter removal

3.1 Ion exchange technology in water treatment

Ion-exchange resins are widely used in different separation, purification, and decontamination processes in water treatment. The most common examples are water softening and water purification.

Water of highest purity is required for electronics, scientific experiments, production of superconductors, and nuclear industry, among others. Such water is produced using ion-exchange processes or combinations of membrane and ion-exchange methods.

The ion exchange process has been around in nature since the beginning of time although it was not observed and quantified until the mid 1800s when sodium forms of naturally occurring zeolites were shown to convert (exchange) ammonium salts in a solution to their sodium species after passing through a bed of the zeolite (which retained the ammonium ions). This process was also shown to be reversible by passing a strong solution of sodium salt through the zeolite, thus stripping the ammonium ion and restoring the bed to its sodium form. It was also demonstrated that "hard" water could be made "soft" by exchanging the hard water ions for sodium. This gave birth to the "softening" process (see Figure 3.1) which was put into commercial application around the turn of the 20th century. Regeneration is performed with common salt.

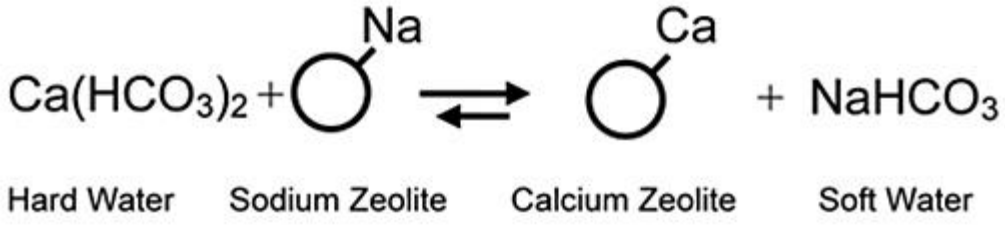

Figure. 3.1. Ion exchange in water softening [18].

After inventing the ion exchange, water de-mineralization process (shown in Figure 3.2) has become very effective, although it was possible to make only through multi-step distillation before.

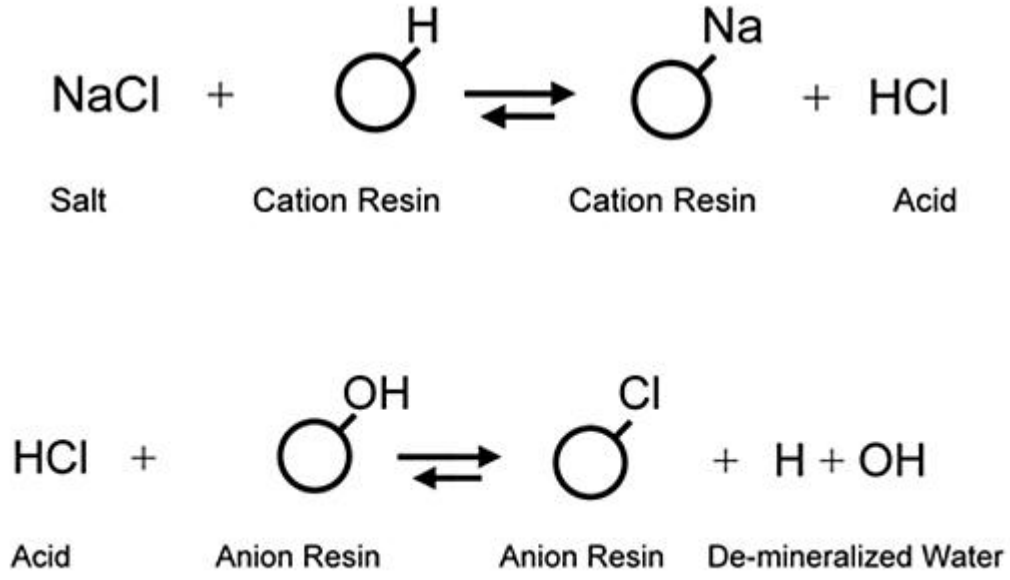

Figure 3.2. Ion exchange in water de-mineralization process

De-mineralization via ion exchange has become the work horse of the high purity water industry. Regeneration is performed with strong acid and caustic soda [18].

3.2 Ion exchange for natural organic matter removal

As it was mentioned above, potable waters containing large amounts of the lower molecular weight forms of humic substances which can be difficult to treat by coagulation processes, especially if the waters are low in turbidity. The smaller molecules are less effectively removed by coagulation and are better taken out by adsorbents or, after oxidative degradation, by biological methods. The use of anion exchange resins to adsorb natural organic matter from drinking water is well known. Quaternary ammonium (QA) resins are normally used in the chloride form or hydroxide, with the ions being replaced by the organic anions. Regeneration is achieved with brine or caustic brine. Ion exchange has been claimed to be more effective than activated carbon, carbonaceous resins or metal oxides for NOM adsorption [19].

Extensive investigations have been proving the efficiency of ion exchange in terms of NOM removal. The efficiency depends on different factors such as NOM concentration, NOM composition, type of IEX resin, empty bed contact time and configuration of the IEX installation [20]. Researchers all over the World are interested in finding the most

accurate balance between the quality of NOM removal from drinking water and expenses for that process. Studies conducted show that the IEX is relatively cost effective, easy to operate and a compact installation can be used due to the short contact times [20].

3.3 Ion exchange resins

During the experiments conducted during this thesis project, two types of resins were tested: strong basic resin A860 and weak basic resin A847. Both resins were produced by the company Purolite. Initially the resins are in CL^- forms; however, resins were recharged into OH^- form to be able to make saturation and regeneration efficiency comparison in different forms.

3.3.1 Strong basic resin A860

Purolite A860 is a macroporous type 1 strong base anion exchange resin with an acrylic matrix. The acrylic matrix ensures excellent removal of organic matter from a water supply in conjunction with their reversible removal upon regeneration. This resin is regenerated very efficiently with lower levels of sodium hydroxide than those required for a polystyrene based type 1 resin, and yet it has a comparable ability to remove weaker acids including carbonic acid and silica. Its use in combination with a polystyrene based resin (for instance in a mixed bed positioned after the anion unit) can often result in the removal of a wider spectrum of organic compounds than either type of anion resin alone, and is particularly resistant to organic fouling, even where loadings are relatively high. [21]

The main physical properties of strong basic resin A860 are listed in Table 3.1 below.

Table 3.1. A860 resin. Physical properties.

Total Capacity (min.)	0.8 eq/l (17.5 Kgr/ft3) (Cl- form)
Moisture Retention	66 - 72 % (Cl- form)
Particle Size Range	300 - 1200 µm
Uniformity Coefficient (max.)	1.7
Reversible Swelling, Cl- → OH- (max.)	20 %
Specific Gravity	1.08
Shipping Weight (approx.)	680 - 730 g/l (42.5 - 45.6 lb/ft3)
Temp Limit, Cl- Form	80°C (176°F)

3.3.2 Weak basic resin A847

Purolite A847 is a unique weak base resin, with a gel acrylic divinylbenzene matrix and tertiary amine functionality. The special properties are associated with the extremely low rinse requirement after regeneration with caustic soda together with an increase in useful operating capacity of up to 10%. Compared to similar resins, Purolite A847 shows excellent resistance to organic fouling, and because of its ability to adsorb and desorb organics efficiently, it can act as a guard column for strong base polystyrene resin that may be placed downstream in a de-mineralization system. Purolite A847 shows unique resistance against osmotic shock attrition as well as being physically resistant to mechanical breakage. Efficiency of regeneration is good, and only 125% to 135% of stoichiometric caustic soda is required to regenerate the exhausted resin. [21]

The main physical properties of weak basic resin A847 are listed in Table 3.2 below.

Table 3.2. A847 resin. Physical properties.

Total Capacity (min.)	1.6 eq/l (34.9 Kgr/ft3) (Free Base form)
Moisture Retention	56 - 62 % (Free Base form)
Particle Size Range	300 - 1200 µm
<300 µm (max.)	1 %
Uniformity Coefficient (max.)	1.7
Reversible Swelling, FB → Cl- (max.)	25 %
Irreversible Swelling (max.)	5 %
Specific Gravity	1.08
Shipping Weight (approx.)	675 - 705 g/l (42.4 - 44.1 lb/ft3)
Temp Limit, Free Base Form	40°C (104°F)

3.4 Water source

Synthetic water was prepared for the experiments; the main components of river water were reproduced: natural organic matter (supplied by International Humic Substances Society), sodium bicarbonate (purity of 100.9%, Fisher Scientific, USA), and sodium chloride (purity of 100.9%, Fisher Scientific, USA). NOM used for the synthetic water preparation was extracted from the Suwannee River water, southern Georgia, USA. The organic matter derived from this river is characterized high aromatic carbon con-

tent and is of predominantly lignin origin [1], thus about 53% of the matter is organic carbon [22].

The composition of the water prepared was the following:

- Deionized water (DI);
- 20 mg/L SR NOM (8 ppm TOC);
- 40 mg/L of NaHCO3;
- 1 mg/L of NaCl;
- 1 mL/L of 0.1 M of NaOH was added to adjust the pH.

The adjusted pH of SR NOM water was about 7 at the room temperature. Between the experiments the water was stored in plastic containers in the cold room, where the temperature was maintained constantly low, so that the composition of the water would not change.

4 Experimental methodology

4.1 Resin preparation

The fresh resin supplied by the manufacturer was washed before being used to remove any possible organics being released from the resin. The resin was washed in an into Erlenmeyer flask by DI water during 24 hours, then filtered and stored in a jar with the lid. The washed resin was directly used in the experiments.

The volume of the resin needed for the experiments was determined by using a graduated cylinder, where the resin was placed and which was filled up with DI water. The water was applied to avoid air gaps in between the resins. Thus, the resin was settled down to the bottom of the cylinder and made a packed column.

4.2 Sampling protocol

All the experiments were conducted using a frequent and careful sampling procedure. Samples were taken at the same time with the experiment by certain interval defined for every experiment. Samples were poured into 40mL amber glass vials and sealed either by a lid or by parafilm. All the vials were carefully labeled. For some experiments samples were duplicated in order to be able to conduct more analysis. Samples were analyzed on the same day or stored in a cold room for further analysis.

4.3 Resin saturation

This section presents a comparison of strong and weak basic resins in terms of NOM removal under multiple loading tests

The test objective was to saturate fresh resin by 700 Bed Volumes (BV) of SR NOM water, the amount required by the resin manufacturer, in a short period of time. The multiple loading test using jar test equipment was applied to resin saturation. Two types of resins in two forms were tested and compared with respect to efficiency: weak basic resin (A847) in chloride and hydroxide forms and strong basic resin (A860) in chloride and hydroxide forms. Samples were taken at the end of each run for further UVA254 and TOC analysis.

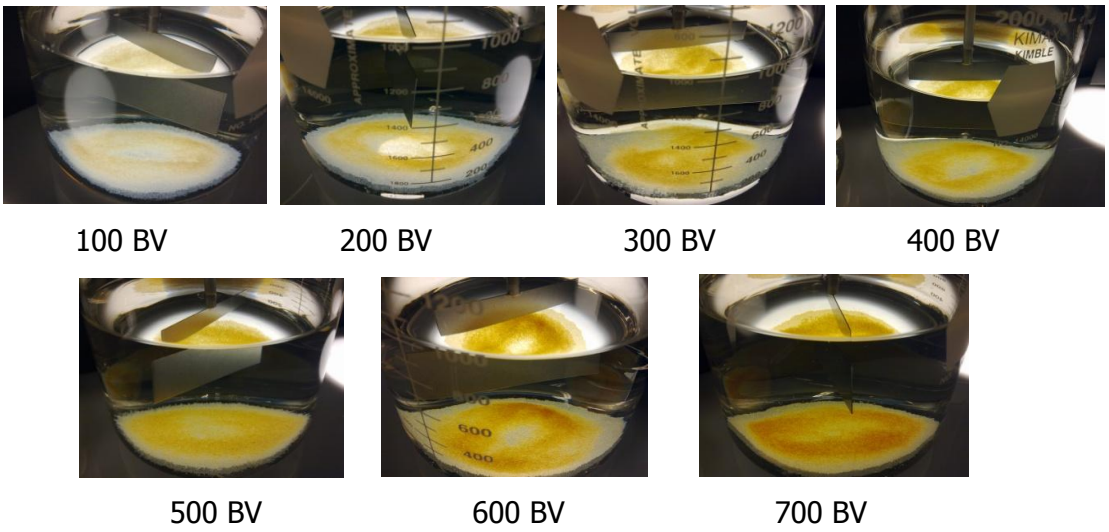

Figure 4.1. Resin coloring during saturation by multiple loading test.

In Figure 4.1 above the resin saturation under multiple loading tests is presented. It is visually observed that resin gains the colour by capturing NOM fractions from the treated water. The thin yellow colour obtained after the first 100 BV became deep yellow when 700 BV was reached.

4.3.1 CL – form resins

Resins A860 and A847 in Cl-form were used to conduct the experiment. A total of 10 mL of each resin were measured for the test, and 14L of SR NOM water was prepared. Resin was mixed with 1L of SR NOM water into separate beakers. Each run lasted 30 minutes with 150 rounds per minute (RPM) vane rotation speed whereupon water was filtered and replaced by a new portion. The procedure was repeated for 7 cycles. Samples were taken into 2 vials of 40mL after each cycle.

4.3.2 OH – form resins

To prepare OH-form resins, A860 and A847 were primarily regenerated by NaOH solution to replace Cl^- by OH^-. A total of 10mL of each OH-form resins were measured and mixed with 1L SR NOM water for saturation. Saturation was conducted by 7 cycles of 30 minutes. Samples were taken into 2 vials of 40mL after each cycle for analysis.

Saturated resin was filtered to remove the SR NOM water residue, was filled with DI water and stored in a jar until regeneration.

During the thesis project, the multiple loading tests were performed 3 times for strong Cl-form resin, 2 times for weak Cl-form resin, 1 time for strong OH-form resin, and 2 times for weak OH-form resin. Further regeneration was implemented in order to evaluate the resin performance and compare of its efficiency under various conditions.

4.4 Regeneration procedure

4.4.1 NaCL regeneration

A total of 10% wt. of brine for regeneration was prepared. 111.11 g of NaCl was mixed with 1 liter of DI water in Erlenmeyer flask and stirred until the salt was totally dissolved. The prepared solution was stored in the flask sealed by parafilm to avoid evaporation.

4.4.1.1 1:10 ratio

A 5 mL of saturated resin were measured and filled in with 20 mL of prepared brine solution. Resin plus brine were stirred into the beaker by the magnetic stirrer on the plate. The beaker of 50 mL was used. The optimal volume of the beaker was matched to obtain the maximum performance of regeneration for certain volume of the brine.

4.4.1.2 1:100 ratio

5 mL of saturated resin were regenerated by 200 mL of brine. The beaker of 200 mL was used for the experiment.

4.4.2 NaOH regeneration

A 4% wt. NaOH solution was prepared for OH-form saturated resin regeneration. 40 g/L of NaOH was dissolved in DI water using Erlenmeyer flask. The solution was stirred on the plate until total dissolving of sodium hydroxide. Safety precautions were followed while preparing, handling and storing the solution.

4.4.2.1 1:10 ratio

A 5 mL of OH-form resin were regenerated by 20 mL of NaOH solution using a 50 mL beaker. The resin was stirred by the magnet on the stirring plate.

4.4.2.2 1:100 ratio

A 5 mL of OH-form saturated resin were regenerated by 200 mL of NaOH regenerant. A 200 mL beaker was used.

Sampling was conducted during the regeneration experiments. The sampling frequency was dependant on the certain experiment. The stirring plate was turned off for some time. After the resin was settled down the sample was taken by using an automatic pipette, then the stirring was continued. The final volume of the regenerated solution was slightly reduced performed an average error of 3%.

5 Data analysis

The samples collected during the experiments were analyzed by several methods: Total organic carbon (TOC) analysis, Ultraviolet–visible (UV) spectroscopy, pH analysis.

5.1 TOC analysis

Total organic carbon (TOC) is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light or air, at 3 to 4 °C for no more than seven days prior to analysis. Alternatively, samples can be acidified with nitric, phosphoric or sulphuric acid to pH 3 or less for longer term storage and to eliminate inorganic carbon [23].

A TOC-V analyzer was used for samples analysis The samples for TOC analysis were collected into dark glass vials, sealed with parafilm and labeled properly. Vials with samples were placed into the equipment cells in random order; vials with DI water were placed between samples for equipment cleaning. The TOC-V analyzer is controlled by the software, where all the analyzed data is collected in a table form.

5.2 Ultraviolet–visible (UV) spectroscopy

The equipment was turned on at least half an hour in advance to let the lamps warm up.

The UV spectrophotometer was set to 254 nm wave length to measure UV absorbance of the prepared samples. Samples were shaken before the analysis to avoid errors due to sedimentation. The measuring cuvette was cleaned by DI water before being filled with the sample and between the samples in order to have the reliable results. Before sample analysis, the clean cuvette was filled up with DI water and the equipment was set up to zero to make a reference. The background absorbance of DI water was about 0.036 cm^{-1}.

The most appropriate range of the absorbance results is between 0 and 1 cm^{-1}. To ensure this, samples with high concentration were diluted.

6 Results and discussion

6.1 Resin saturation

This section presents and discusses the results of the multiple loading tests conducted to compare the NOM removal performance of different strong and weak resin types.

6.1.1 CL – form resins

Figure 6.1 shown below provides the comparison of weak and strong basic resins in terms of NOM removal in multiple loading tests. The comparison is based on the data obtained from the TOC and UVA analyses of the samples. The comparison of NOM removal from the SR NOM water is presented as a function of bed volumes with A860 and A847 resins.

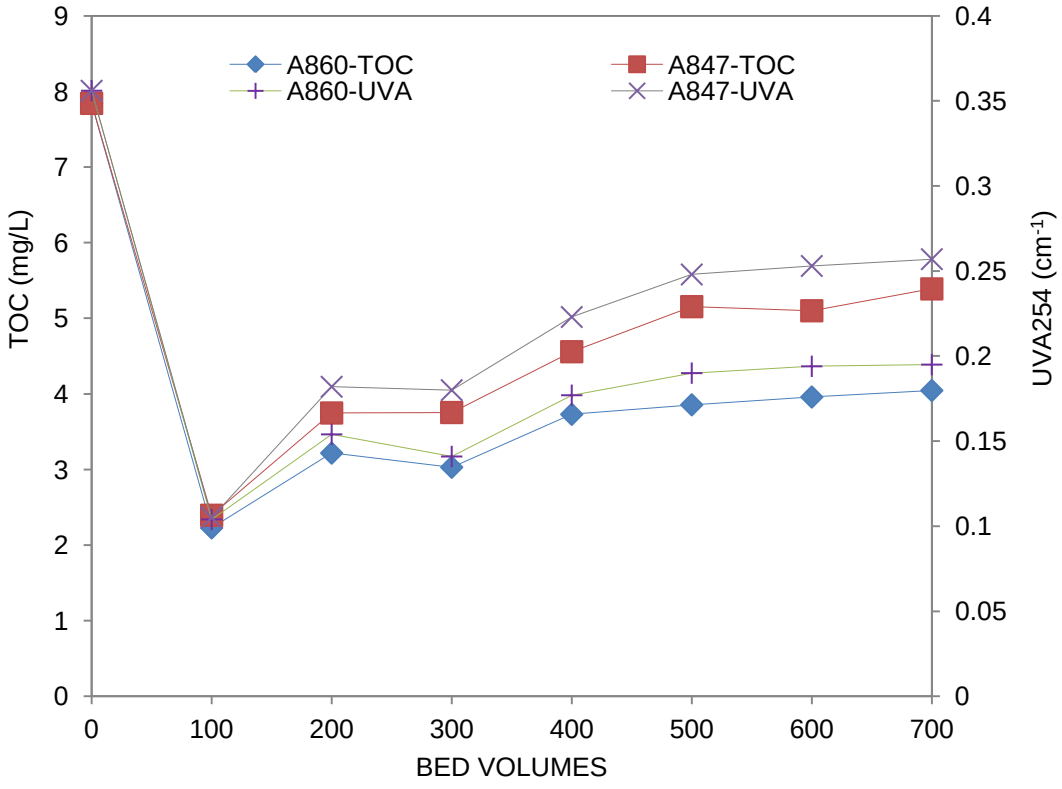

Figure 6.1. Comparison of A860 and A847 resins in terms of NOM removal. First experiment.

Several experiments on Cl-form resin saturation by multiple loading were done. The saturation behavior of the second experiment is presented in Figure 6.2 below.

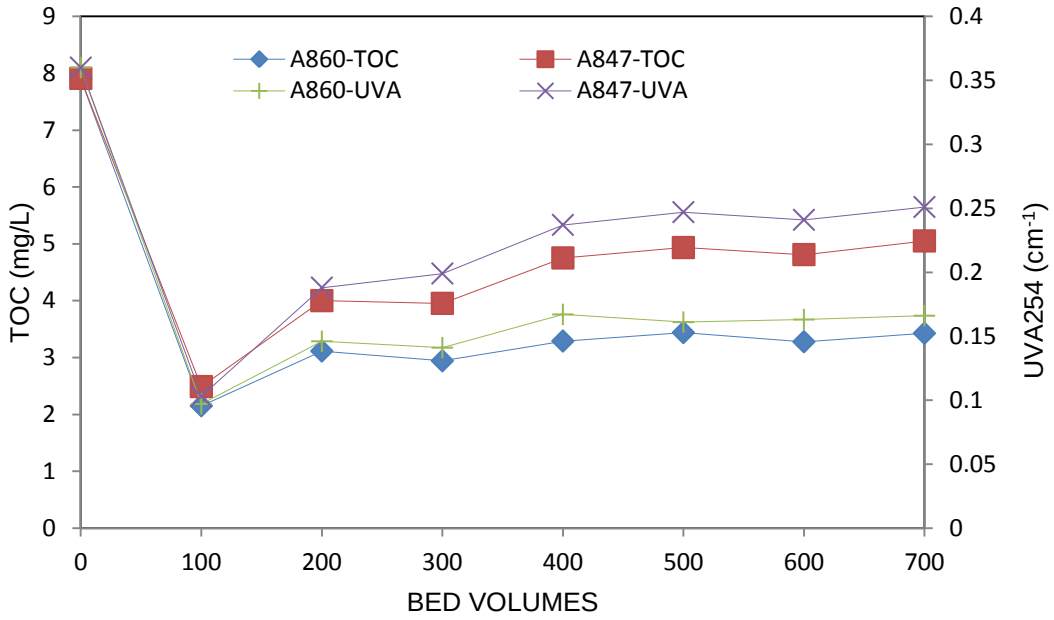

Figure 6.2. Comparison of A860 and A847 resins in terms of NOM removal. Second experiment.

The graphs plotted above show that the behavior of the data is similar for all three loadings of Cl-form resin saturation. Average data of three loadings is presented in Figure 6.3.

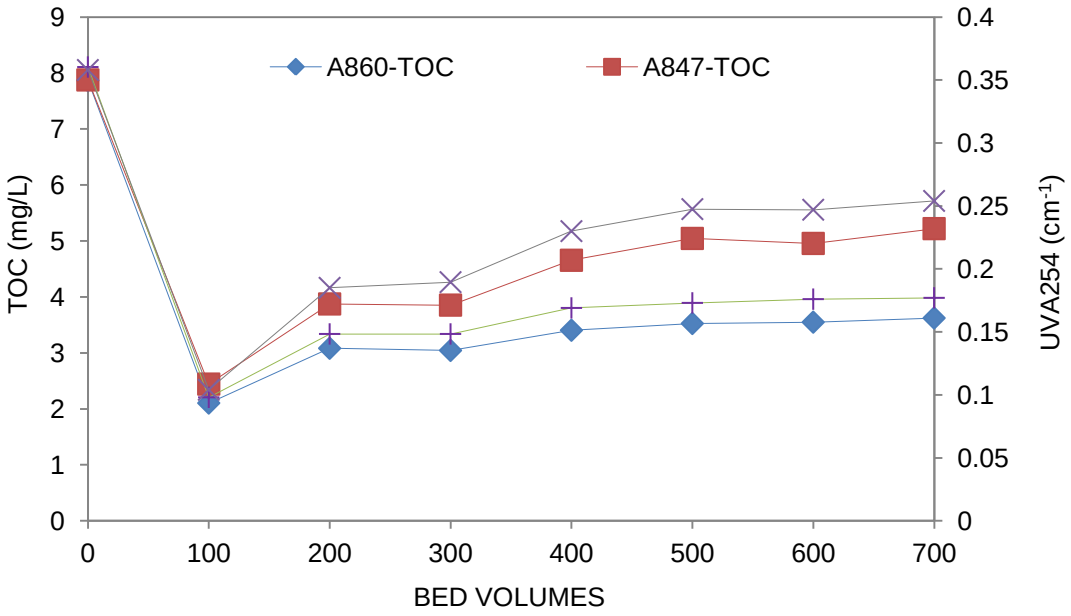

Figure 6.3. Average Cl-form resin saturation data from three loadings.

On the basis of the above graphs, it can be concluded that during the first loading the results show the rapid NOM adsorption for both resins. During 7 cycles a reduction of NOM adsorption was noticed. For A860 resin TOC removal was reduced from 72% to 48%, and for A847 from 69% to 31%. This pattern can be attributed to the difficulty of NOM penetration into the pores of the resin.

Also, it was observed that the performance in terms of residual TOC concentration by the bed volumes is higher for A860 Cl-form resin than for the A847 Cl-form resin. Although the values of TOC concentration at 100 BV are very close to both resins, a difference of 17% was achieved up to 700 BV (TOC removal of A860 is 17% higher than that of A847 resin).

UVA absorbance data observed is confirming the TOC data trend variation for A860 and A847 resins. A860-UVA has shown a 25% reduction and A847-UVA a 43% reduction up to the 7^{th} cycle in terms of NOM removal.

6.1.2 OH – form resins

Figure 6.4 below shows a comparison of the efficiency of NOM removal from SR NOM water between strong basic OH-form resin and weak basic OH-form resin. The figure compares two resins in terms of residual organic matter in water samples after each 100 bed volumes of water treated.

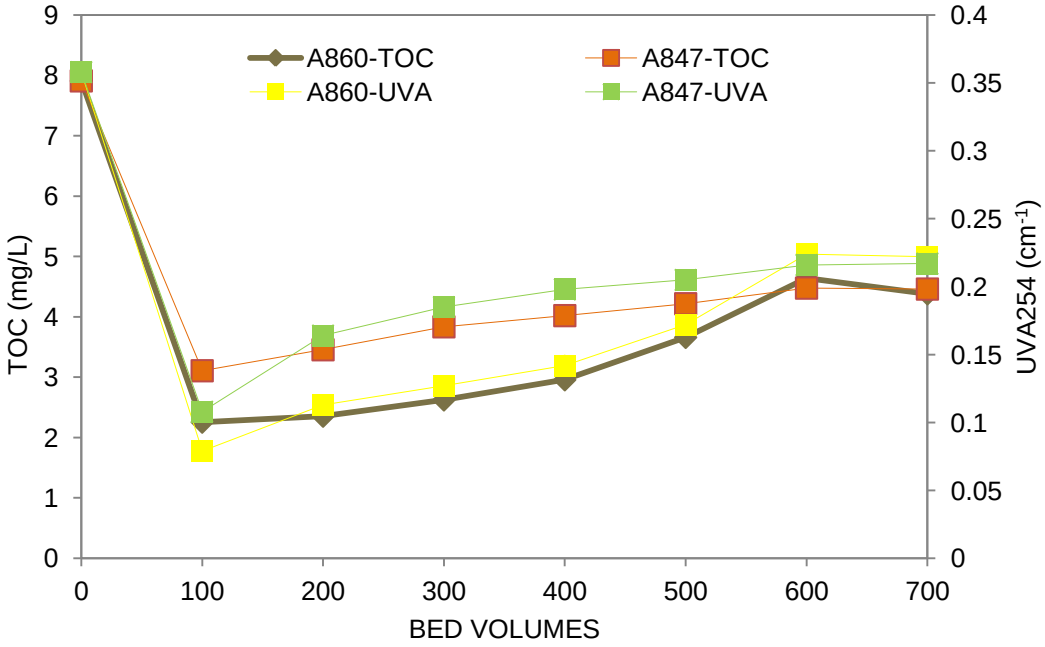

Figure 6.4. OH-form resins. Weak and strong resin efficiency comparison.

The result of UVA254 absorbance for strong basic resin has shown about 12% higher penetration of NOM to the pores of the resin for the first 5 loadings. Nevertheless, at the point of 600 BV the residual amount of NOM seems to be equal for both resins.

Approximately the same pattern was observed in the TOC analysis of the samples. The removal of strong basic resin was approximately 12% higher, although by the sixth loading, weak basic resin shows an approximately 1% higher removal rate.

The saturation of strong basic resin appears to be faster and the performance decreases by the sixth loading, whereas weak basic resin is saturated gradually and shows stable performance during all seven loadings.

6.1.3 CL-form vs. OH-form resins

The comparison of the resin saturation results are shown in Figure 6.5 below. The figure presents the average UV absorbance release results of weak and strong basic resins in Cl- and OH-forms.

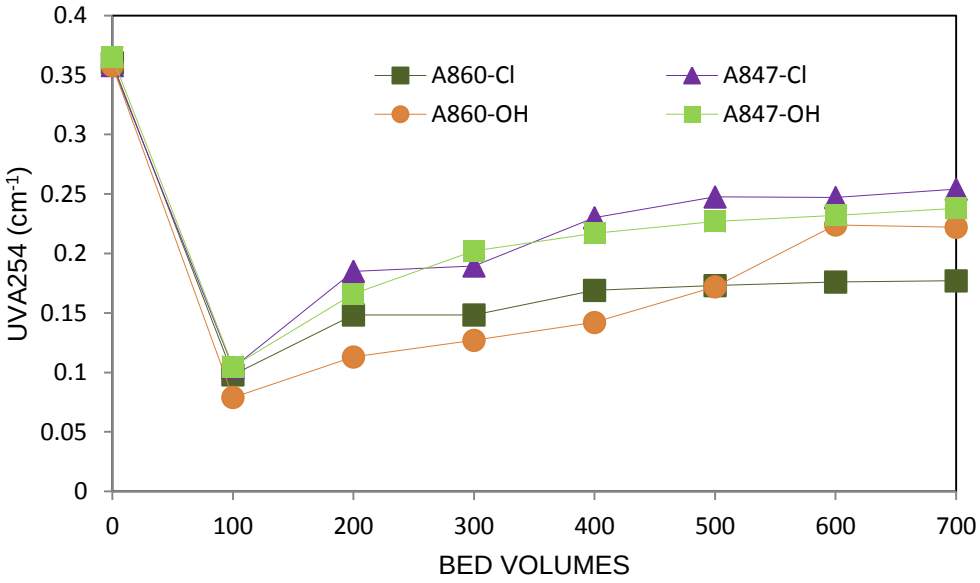

Figure 6.5. Weak Cl- and OH-form vs. strong Cl- and OH-form resins saturation comparison by UV absorbance.

The comparison data shows a rapid reduction in UV absorbance after the first run by 71% in average for 3 resins, accept for A860OH, which exhibited a reduction of 78%. During the next loadings, the UV absorbance of all 4 resins increased, which indicates the deceleration of NOM penetration into the pores of the resin.

The strong basic resin in OH-form shows the highest performance until 400 bed volumes: the NOM reduction achieved ranged from 78% to 60% and decreased to 38% at 700 bed volumes, which is, in general, about 40% reduction during 7 cycles. However, the strong basic resin in Cl-form shows an 8% difference in UV absorbance from 200 to 700 BV, and 22% NOM reduction altogether during 7 cycles.

The weak basic resins in both Cl- and OH-forms have presented larger percentages of UV absorbance, which is the evidence for higher NOM residual in the treated samples. During loadings from 200 to 700 bed volumes, the removal percentage of resin in Cl-form dropped from 48 to 29, and the removal percentage of resin in Cl-form fell from 54 to 36.

To summarize, the strong basic resin shows the most consistent percentage of NOM removal from the samples; moreover, it has shown the highest percent of removal at the point of 700 BV.

6.2 Regeneration

6.2.1 NaCl at different volumes

The table below presents UVA absorbance data collected from the regeneration experiment of resin, saturated on March 22nd by SR NOM water. Regeneration was conducted in three runs by using 10% brine in two different ratios.

The data was combined and plotted into a graph to illustrate the difference between the observations (see Figure 6.6. below).

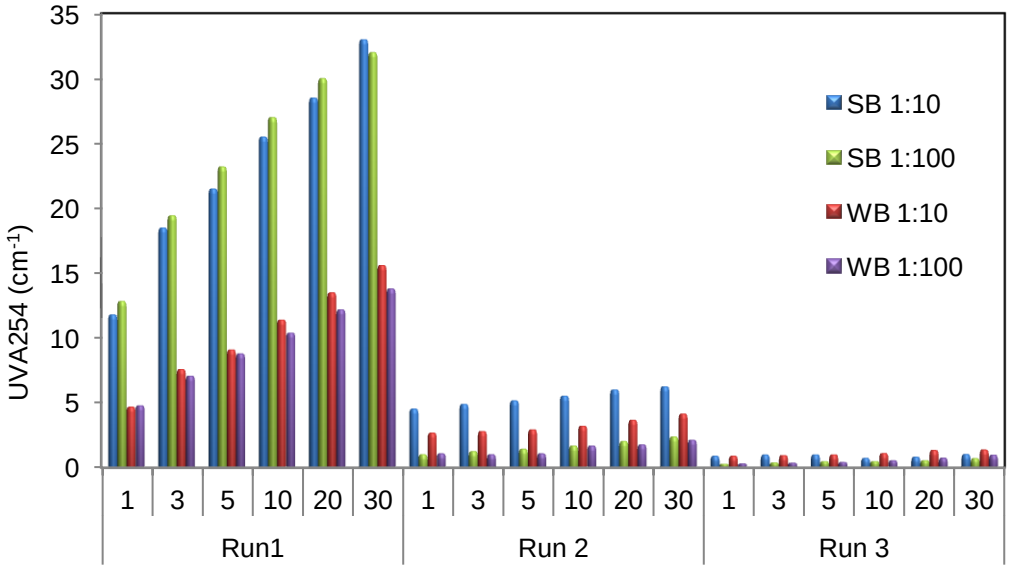

Figure 6.6. Weak basic and strong basic resin regeneration comparison at different volumes. 10% wt. NaCl Regeneration.

Based on collective UV absorbance release, the comparison data shows approximately 55% higher performance of NOM releasing out of the strong basic resin in both ratios rather than the weak basic resin during the first run, whereas the difference between the ratios within the type of resin was very slight: the 1:10 ratio was about 4% smaller than the 1:100 ratio for strong basic resin; however, for weak basic resin, the 1:10 ratio shows 8% higher performance than the 1:100 ratio.

The situation has changed during the second run: the 1:10 ratio shows higher performance for both resins: the performance of strong resin was 40% higher than that of weak resin. The difference in NOM releasing within the resins was observed to be 70% for strong resin, with highest performance at the 1:10 ratio and 55% for weak resin with highest performance at the 1:10 ratio.

During the 3rd run, the situation has changed in the last 3 samplings. The 1:10 ratio of weak basic resin shows the highest performance.

6.2.2 NaOH at different volumes

Figure 6.7 presents the data obtained from OH-form resin regeneration experiment by using a 4% wt. NaOH regenerant. The resin was saturated by SR NOM water on March 18th.

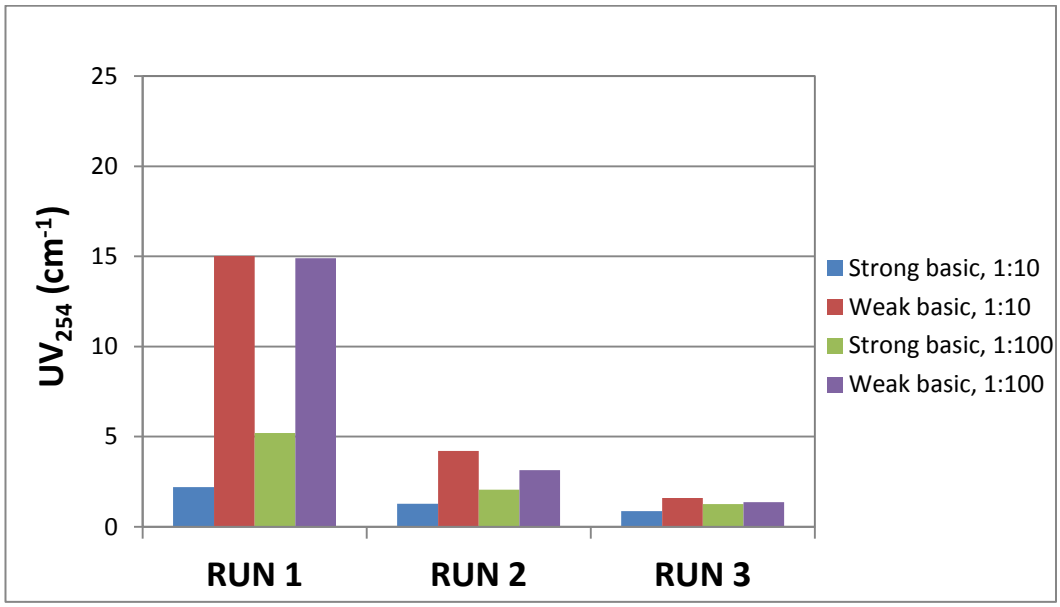

Figure 6.7. Weak basic and strong basic resin regeneration comparison at different volumes. 4% wt. NaOH Regeneration.

The result of the first run of regeneration experiment shows much higher performance of weak basic resin than strong basic resin at both ratios. During the second run, the NOM releasing out of weak basic resin was still higher, but the difference between weak and strong resin decreased from an average of 75% to an average of 55%.

The cumulative results between strong basic and weak basic resins are presented on the Figure 6.8 below.

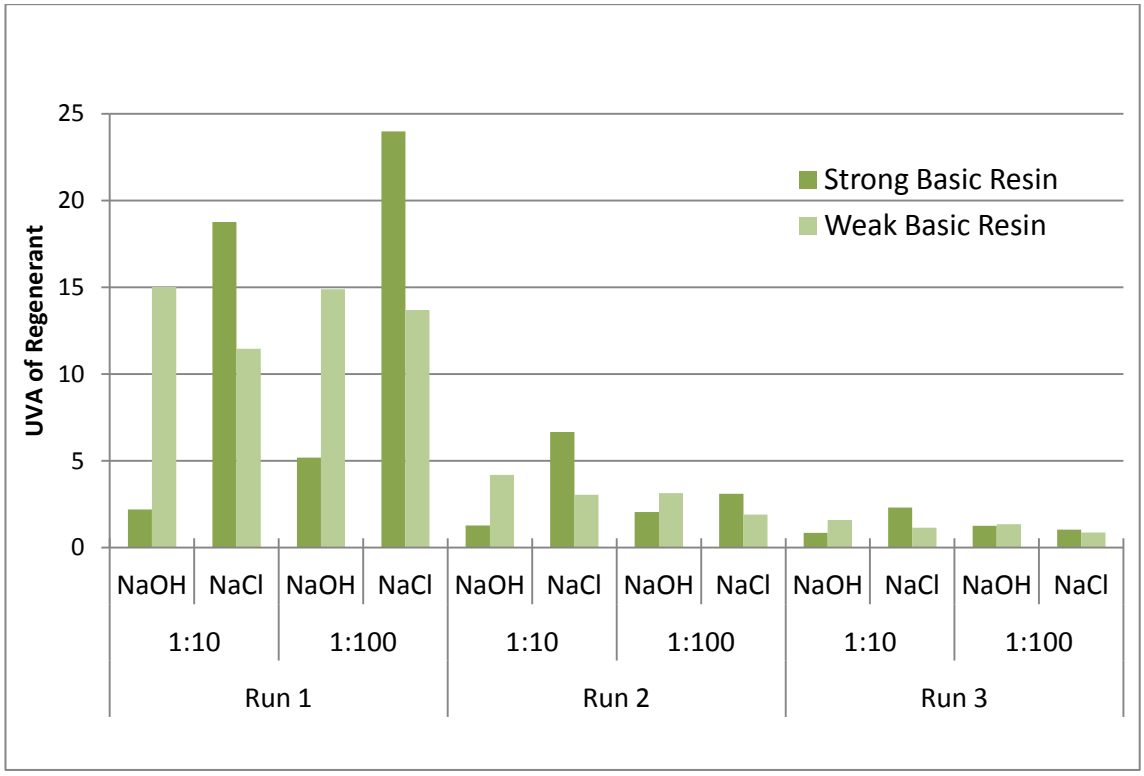

Figure 6.8. Weak basic and strong basic resin regeneration comparison in different forms and at different volumes.

During the first run, the cumulative resin comparison showed the highest resin regeneration performance for strong basic resin in Cl-form at the 1:100 ratio. Although by the second run the strong basic resin in Cl-form at 1:10 ratio showed the highest performance.

7 Conclusion

It was found during the saturation experiments that strong basic resin in Cl-form has more rapid penetration of NOM compounds than weak basic resin in Cl-form. A similar tendency was observed during regeneration process by 10% wt. NaCl: the releasing of organic compounds was faster in case of strong basic resin in Cl-form.

During the resin saturation, strong basic resin in OH-form has shown higher performance than weak basic resin, although in the regeneration by 4% wt. NaOH the weak basic resin was more productive.

Overall, during the resin saturation and regeneration experiments, the strong basic resin in Cl-form has shown more efficient and more gradual results than the other being compared resins.

The results achieved during the experiments could be applied to producing a pilot scale installation. The further analysis is needed in order to be able to evaluate resin performance in larger scale.

References

1. Treavor H. Boyer, Chapel Hill. Removal of natural organic matter by anion exchange: multiscale experimentation and mathematical modeling [Internet], 2008. [Cited on 2014 April 10] Available from: http://books.google.fi/books?id=E-Yu6PLJi2oC&pg=PA14&dq=ion+exchange+natural+organic+matter&hl=en&sa=X&ei=PKNDU9y3Fqe6ygPj_YLgAQ&ved=0CDcQ6AEwAA#v=onepage&q=ion%20exchange%20natural%20organic%20matter&f=false
2. Mary Drikas. Long term case study of MIEX pre-treatment in drinking water; understanding NOM removal [Internet], 2010. [Cited on 2014 April 10] Available from: www.sciencedirect.com
3. Hugues Humbert. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water [Internet], 2007. [Cited on 2014 April 10] Available from: www.sciencedirect.com
4. E.R. Cornelissen. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions [Internet], 2007. [Cited on 2014 March 20] Available from: www.sciencedirect.com
5. Anu Matilainen. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment [Internet], 2011. [Cited on 2014 March 21] Available from: www.sciencedirect.com
6. Billy H. Kornegay. Natural organic matter in Drinking water: recommendations to water utilities. AWWA Research Foundation and American Water Works Association, USA [Internet], 2000. [Cited on 2014 March 15] Available from: http://books.google.fi/books?id=rVb-EL1OBToC&printsec=frontcover&dq=natural+organic+matter&hl=en&sa=X&ei=HKEVU9eUDsPOygPYk4GAAw&ved=0CCoQ6AEwAA#v=onepage&q&f=false
7. Disinfection Byproduct Health Effects, Environmental protection agency of the United States [Internet]. [Cited on 2014 March 15] Available from: http://www.epa.gov/enviro/html/icr/dbp_health.html
8. Andrei A. Zagorodni. Ion Exchange materials. Properties and applications [Internet], 2007. [Cited 05 June 2013]. Available from:

http://books.google.fi/books?id=XfDFKI3I74MC&pg=PA1&source=gbs_toc_r&cad=4#v=onepage&q&f=false

9. Teh Fu Yen. Environmental chemistry: Chemical Principles for Environmental Processes, 1999, Vol. 4B. New Jersey, Prentice Hall PTR.

10. Friedrich Helfferich. Ion Exchange [Internet], 1995, New York, Dover Publications Inc. [Cited on 2014 March 15] Available from: http://books.google.fi/books?id=F9OQMEA88CAC&printsec=frontcover&dq=Ion+Exchange&hl=en&sa=X&ei=tbchU831BM6qhAetqYHwDg&redir_esc=y#v=onepage&q=Ion%20Exchange&f=false
11. C.E. Harland. Ion Exchange: Theory and Practice, 2nd edition [Internet], 1994 The Royal Society of Chemistry, UK. [Cited on 2014 March 15] Available from: http://books.google.fi/books?id=qxEVHpvkmZsC&printsec=frontcover&dq=Ion+Exchange&hl=en&sa=X&ei=tbchU831BM6qhAetqYHwDg&redir_esc=y#v=onepage&q=Ion%20Exchange&f=false
12. R. Kellner, J.-M.Mermet, M.Otto, H.M.Widmer. Analytical Chemistry, 1998, WILEY-VCH Verlag GmbH, Germany.
13. Lindsay Erin Anderson. Anion exchange resin technology for natural organic matter removal from surface water, Dalhousie University Halifax, Nova Scotia, Canada, 2013.
14. Manual for TOC-V Series, Shimadzu Scientific Instruments [Internet]. [Cited on 2014 March 17] Available from: http://www.ssi.shimadzu.com/products/literature/toc/toc-v-series.pdf
15. Total Organic Carbon, Water/Wastewater Distance Learning Website [Internet]. [Cited on 2014 March 17] Available from: http://water.me.vccs.edu/exam_prep/TOC.html
16. TOC Analyzers [Internet]. [Cited on 2014 March 17] Available from: http://EzineArticles.com/1480842
17. TOC analyzer picture [Internet]. [Cited on 2014 March 17] Available from: http://www.comfortech.com.hk/store/image/TOC-V%20CPH.gif
18. The working principle of resin, Ji Hai Resin [Internet], 2013. [Cited on 2014 April 15] Available from: http://www.jh-resin.com/en/news.php?classid=52&id=103

19. Brian Bolto, David Dixon, Rob Eldridge, Simon King, Kathryn Linge. Removal of natural organic matter by ion exchange [Internet], 2002. [Cited 05 June 2013] Available from: http://ac.els-cdn.com/S0043135402002312/1-s2.0-S0043135402002312-main.pdf?_tid=7295041c-cdd0-11e2-883a-00000aab0f26&acdnat=1370430773_f734623a37d124c830e1e9d478b68d28;
20. Anke Grefte Thesis: Removal of Natural Organic Matter Fractions by Anion Exchange. Impact on drinking water treatment processes and biological stability, 2013.
21. Purolite, IEX resins [Internet]. [Cited 04 June 2013] Available from: https://puroweb.purolite.com/default.aspx?RelID=606288&ProductID=225
22. IHCC., Suwannee River NOM [Internet], 2009. [Cited 25 March 2013] Available from: http://www.humicsubstances.org/sources.html
23. Water Quality, Definitions, Concepts and Analytical Measurements. Ministry of Environment, British Columbia, Canada [Internet]. [Cited 25 March 2014] Available from: http://www.env.gov.bc.ca/wat/wq/BCguidelines/orgcarbon/definitions.html